Metal-Organic Frameworks for Adsorbed Natural Gas Fuel Systems

Hong-Cai “Joe” Zhou
Department of Chemistry
Texas A&M University
US primary energy consumption by fuel, 1980-2035 (quadrillion Btu per year)

Coal and oil (and other nonrenewable liquid fuels) constitute nearly 60% of total energy consumption in the U.S., with the greatest portion of energy generated used for transportation. (~70% of all oil consumed is used for transportation)

Delivered energy consumption by sector, 1980-2035 (quadrillion Btu)

The U.S. imports 22% of its energy sources, and ~50% of its oil supply.

US liquid fuel supplies, 1970-2035 (million barrels per day)
Natural Gas (NG) as an Energy Source

**Advantages**
- Inexpensive
- High octane rating (RON ~ 130)
- Reduction in harmful emissions
- Gravimetric energy density comparable to gasoline (50.0 MJ/kg v. 44.5 MJ/kg)

**Challenges**
- CO₂ emissions
- Low volumetric energy density

Benzene – up to 100%
VOCs – up to 92% or more
SO₂ – 83%
CO – 40 %
CO₂ – 25%
NOₓ – 10%
Particulate matter – over 90%, compared to diesel

* Depending on the characteristic of the adsorbent.

## Current NG Storage Methods

**Liquefied Natural Gas (LNG)**

- Volumetric energy density ~72% of gasoline
- Stored under cryogenic conditions, 112 K and 1 bar
- Susceptible to boil off and pressure buildup
- Requires special handling procedures/storage tank

**Compressed Natural Gas (CNG)**

- Compressed to 200-300 bar
- Maximum energy density ~26% of gasoline
- Requires special heavy, bulky cylinders
- Requires expensive, multi-stage compressor for filling
Adsorbed Natural Gas

- High surface area/micropore volume materials can enhance packing density of methane
- Operate under preferred conditions; ambient temperature and < 35 bar
- Can be stored in light weight, shapeable fuel tanks
Properties of Ideal ANG Systems

- High adsorption capacity
- Good uptake/release kinetics
- Microporous
  - Maximum storage, pore size = 7.6 Å
  - Maximum deliverable capacity, pore size = 11.4 Å
- High packing density
- Low heat of adsorption (18.8 kJ/mol)
- Good mass transfer properties
- Hydrophobic pore surfaces
- Inexpensive
Traditional Porous Sorbents

• Carbonaceous materials
  ▫ Advantages: Inexpensive and theoretical delivery capacity of 220 v(STP)/v
  ▫ Disadvantages: Wide pore size distribution and lack of control of pore size

• Zeolites
  ▫ Advantages: High packing density; regular, ordered pores
  ▫ Disadvantages: Low micropore volume and hydrophilic
MOFs

- Crystalline materials with regular, ordered pores
- Tunable pore size
- High surface area and pore volume
- Ability to tailor functionality and post-synthetically modify system
- Primarily weak host-guest interactions
- Limitless metal-ligand combinations
Synthesis Flowsheet

Solution Terephthalic acid

Solution Zinc-Source (e.g. Oxide, Nitrate, Acetate)

Precipitation, Crystallization

Recycling Solvent

Filtration, Drying

Processing Shaping
# Methane Uptake in Select Materials

DOE target: 180 v/v (ambient temperature, pressure ≤ 35 bar)

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area</th>
<th>Pore volume</th>
<th>Density</th>
<th>Ambient temperature methane uptake wt %</th>
<th>Ambient temperature methane uptake v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCN-14 Cu₂(adip)</td>
<td>1753</td>
<td>0.87</td>
<td>0.83</td>
<td>16.0 (35 bar)</td>
<td>230</td>
</tr>
<tr>
<td>PCN-11 Cu₂(sbtc)</td>
<td>1931</td>
<td>0.91</td>
<td>0.75</td>
<td>14.1 (35 bar)</td>
<td>171</td>
</tr>
<tr>
<td>HKUST-1 Cu₃(btc)₂</td>
<td>692-1944</td>
<td>0.76</td>
<td>0.88</td>
<td>(35 bar)</td>
<td>160</td>
</tr>
<tr>
<td>Zn₂(bdc)₂dabco</td>
<td>1448</td>
<td>0.75</td>
<td>0.87</td>
<td>14.3 (75 bar)</td>
<td>210</td>
</tr>
<tr>
<td>NiMOF-74 Ni₂(dhtp)</td>
<td>599-1070</td>
<td>0.54</td>
<td>1.206</td>
<td>(35 bar)</td>
<td>190</td>
</tr>
<tr>
<td>UTSA-20 Cu₃(bhb)</td>
<td>1156</td>
<td>0.63</td>
<td></td>
<td>(35 bar)</td>
<td>178</td>
</tr>
<tr>
<td>COF-103</td>
<td>5230</td>
<td>2.05</td>
<td>0.38</td>
<td>31.0 (100 bar)</td>
<td>260</td>
</tr>
</tbody>
</table>
Identifying Characteristics of MOFs with High Methane Uptake
At low pressure methane tends to adsorb near unsaturated metal centers (UMCs), then adsorbs in “tight” locations that maximize methane-framework interactions, when UMCs are fully occupied.

Saturation of UMCs in MMOF-74 are calculated to result in uptake capacities from 160 – 174 v/v

UMCs in UTSA-20 were calculated to attribute to a maximum storage capacity of only 89 v/v, about half of the total uptake.

The remaining uptake is attributed to uptake in the channel-like pores, exhibiting enhanced interactions due to methane being sandwiched between two linkers.
IRMOF-993: computations show methane storage capacity > 180 v/v.

PCN-13 SBUs: steric bulk from anthracene forces distortion of the Zn₄O SBU.
PCN-14: Extending from anthracene for enhanced methane uptake
Designing New Materials
PCN-12 and 12’

H$_2$ Uptake Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Uptake</th>
<th>Material</th>
<th>Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCN-12</td>
<td>3.05</td>
<td>PCN-10</td>
<td>2.34</td>
</tr>
<tr>
<td>MOF-505</td>
<td>2.59</td>
<td>Mn-BTT</td>
<td>2.25</td>
</tr>
<tr>
<td>PCN-11</td>
<td>2.55</td>
<td>Cu$_2$(qptc)</td>
<td>2.24</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>2.54</td>
<td>PCN-6</td>
<td>1.90</td>
</tr>
<tr>
<td>Cu$_2$(tptc)</td>
<td>2.52</td>
<td>PCN-9</td>
<td>1.53</td>
</tr>
<tr>
<td>Cu-BTT</td>
<td>2.42</td>
<td>PCN-6</td>
<td>1.35</td>
</tr>
<tr>
<td>PCN-12'</td>
<td>2.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bulky Aromatic Linkers

\[
\text{Initial Compound} \xrightarrow{\text{Sn, HOAc, HCl}} \text{Intermediate} \xrightarrow{\text{Br}_2} \text{Bulky Aromatic Linker 1} \xrightarrow{1) \text{BuLi}} \text{Bulky Aromatic Linker 2} \xrightarrow{2) \text{CO}_2} \text{Bulky Aromatic Linker 3} \xrightarrow{3) \text{H}_3\text{O}^+} \text{Final Compound}
\]
\[\text{Mn}^{2+}/\text{Co}^{2+} + \text{H}_2\text{BADC}\]

\[\text{Mn}^{2+} + \text{H}_2\text{BADC} \text{ (lower pH)}\]

\[\text{Co}^{2+} + \text{H}_2\text{BADC} + \text{BIPY}\]
Mn$^{2+}$ + H$_2$BADB

View along [1 0 0] direction 4 × 16 Å$^2$

View along [0 1 0] direction 6 × 13 Å$^2$
Bulky Aromatic Linker Series
Enhancing the Stability of MOFs: ZrMOFs
Selected ligands

L0
HOOC-[\(R_1\)]-[\(R_2\)]-[\(R_3\)]-COOH

L3
HOOC-[\(R_1\)]-[\(R_2\)]-[\(R_3\)]-[\(R_4\)]-COOH

L4
HOOC-[\(R_1\)]-[\(R_2\)]-[\(R_3\)]-[\(R_4\)]-[\(R_5\)]-COOH

L1
HOOC-[\(R_1\)]-[\(R_2\)]-[\(R_3\)]-[\(R_4\)]-[\(R_5\)]-COOH

L5
HOOC-[\(R_1\)]-[\(R_2\)]-[\(R_3\)]-COOH

And others
Synthesis of a series of Zr-MOFs

- Simulated from single crystal data
- Optimized synthesis for L1
- Try for L2
- Try for L3
- Try for L4
Looking to the Future
The Call for Natural Gas

ARPA-E Project
Leading: Texas A&M
Team: GM, RTI, LBNL
Funding: $3,000,000

• significantly improving the volumetric energy density of methane

• driving down the cost of vehicular use of natural gas by eliminating expensive compressors or specialized storage tanks necessary for compressed and liquefied natural gas

• reducing safety and environmental concerns associated with compressed and liquefied natural gas

• significantly advancing technologies for application in natural gas powered vehicles

Functional ANG fuel tank with integrated thermal management system
**Technology Summary**

- Simultaneous development of new sorbents and ANG fuel tank design led by computational models with feedback loop
- Inexpensive, effective, and stable sorbents designed based upon “optimal space filling” of methane within cavities (length tuned to 3.8 Å, \( n \) is an integer)
- Densification of sorbent through formation of novel module-based ANG fuel tank system with integrated heat exchangers

**Technology Impact**

- Decrease costs and safety concerns associated with use of natural gas in light-duty vehicles
- Reduce dependence on foreign oil; increases U.S. energy independence

**Proposed Targets**

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric energy density</td>
<td>9.15 MJ/L(_{\text{sorbent}}) (PCN-14; 290 K, 35 bar)</td>
<td>&gt; 12.5 MJ/L(<em>{\text{sorbent}}); &gt; 9.2 MJ/L(</em>{\text{system}}) (near ambient T, 35 bar)</td>
</tr>
<tr>
<td>Sorbent cost</td>
<td>&gt; $10,000 / kg (top performing materials)</td>
<td>&lt; $10 / kg</td>
</tr>
<tr>
<td>Impurity resistance</td>
<td>Unknown</td>
<td>&gt; 80% of initial capacity after 100 cycles</td>
</tr>
</tbody>
</table>

**Schematic of potential thermal management system incorporated with ANG fuel tank**

**Moisture stable porous materials**

- PPN-4 \( (S_{\text{ret}} = 6500 \text{ m}^2/\text{g}, 388 \text{ mg/g}) \)
- Carbon \( (S_{\text{ret}} = 3100 \text{ m}^2/\text{g}) \)
- Zeolite \( (S_{\text{ret}} = 1000 \text{ m}^2/\text{g}) \)

**Economical polymerization strategies for preparation of novel PPNs syntheses.**

1) Copper-catalyzed alkyne self-coupling (Eglinton);
2) Imide condensation;
3) Substitutive polymerization
Acknowledgements

- NSF
- Welch Foundation
- GM

- Chevron
- DOE
- Texas A&M University
Electricity generation by fuel, 1990-2035 (trillion kilowatthours per year)